

09/575094US02  
09/666,642  
Art Unit: 1711

20

## REMARKS

1. *Amendments to the Specification*

Replacement paragraphs correcting the misspelling of the word naphthalate in the paragraphs at page 4, lines 3-13, page 6, lines 21-30, page 7, lines 1-10, and page 10, lines 13-19 are kindly requested. No new matter has been introduced by the replacement of the above-referenced paragraphs as “[a]n amendment to correct an obvious error does not constitute new matter where one skilled in the art would not only recognize the existence of the error in the specification, but also recognize the appropriate correction.” MPEP § 2163.07 II.

2. *Status of Claims*

After the amendments to the claims, claims 1-4, 7, 10-11, 15-30, 33, 36-37, 41-66, 70-73, 76, 79-80, 84-91, 94, 97-98, and 102-115 are pending in the application. Claims 1-4, 7, 10-11, 15, 17-30, 33, 36-37, 41, 43-66, 70-73, 76, 79-80, 84, 86-91, 94, 97-98, 102-113, and 115 are pending and under consideration. Claims 16, 42, 85, and 114 are pending but withdrawn. Claims 5-6, 8-9, 12-14, 31-32, 34-35, 38-40, 67-69, 74-75, 77-78, 81-83, 92-93, 95-96, and 99-101 are cancelled.

3. *Amendments to the Claims*

Independent claims 1, 28, 72, 89, and 90 have been amended to incorporate the oxygen scavenging polymer limitations of claims 5 and 9 into the independent claims. Additionally, independent claims 1, 28, 72, 89, and 90 have been amended to stipulate that the active oxygen barrier composition minimally comprises a blend of an oxygen barrier polymer and an oxygen scavenging polymer. Support for this later limitation can be found on page 5, lines 18-20, among other places, of the patent application.

Claims 5, 9, 32, 35, 75, 78, 93, and 96 have been canceled as these dependent claims have been incorporated into their respective independent claims. Claims 7, 10, 33, 36, 76, 79, 94, and 97 have been amended to depend from the appropriate independent claim (claim 1, 28, 72, or 90) to maintain proper claim dependency.

09/575094US02  
09/666,642  
Art Unit: 1711

21

The Office Action dated June 24, 2005, indicated that claims 12-14, 38, 67-69, 81-83, and 99-101 were withdrawn from consideration while claims 39 and 40 were pending and under consideration. Review of Applicants' records indicate that claims 12-14, 38-40, 67-69, 81-83, and 99-101 were canceled in the RCE filed on October 12, 2004, in response to the Office Action dated May 10, 2004. By this Office Action Response, Applicants reaffirm that claims 12-14, 38-40, 67-69, 81-83, and 99-101 are canceled.

4. *Rejections Under 35 U.S.C. §112*

Claims 111, 112, and 114 have been rejected under 35 U.S.C. §112 as "failing to comply with the written description requirement" for containing "subject matter which was not described in the specification in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention." Applicants respectfully traverse this rejection.

Applicants respectfully submit that by this Office Action Response the appropriate paragraphs of the specification have been replaced with paragraphs having the correct spelling of the word "naphthalate" and that one skilled in the art would readily recognize this misspelling. The MPEP at 2163.07 II states that "[a]n amendment to correct an obvious error does not constitute new matter where one skilled in the art would not only recognize the existence of the error in the specification, but also recognize the appropriate correction." Applicants respectfully request that the 35 U.S.C. §112 rejection of claims 111, 112, and 114 be withdrawn.

Claims 1-4, 6-11, 15, 17-30, 32-37, 41, 43-66, 70-73, 75-80, 84, 86-91, 93-98, 102-113 and 115 have been rejected under 35 U.S.C. §112, first paragraph, as "containing subject matter which was not described in the specification in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention." Specifically, page 2 of the Office Action dated June 24, 2005, asserts, "[t]he limitation 'consists essentially of a polyethylenic backbone' was not present in the specification as filed." Applicants respectfully traverse this rejection.

Applicants believe that the subject matter of the limitation "consists essentially of a polyethylenic backbone" is described in the specification even though the limitation is not used in *haec verba* within the specification. However, to advance the prosecution of this application and more distinctly claim the

09/575094US02  
09/666,642  
Art Unit: 1711

22

subject matter which the Applicants regard as the invention, the Applicants have amended the claims in a manner that removes the limitation "consists essentially of a polyethylenic backbone" from independent claims 1, 28, 72, 89, and 90. Applicants respectfully request that the 35 U.S.C. §112 rejection of the pending claims, in relation to the limitation "consists essentially of a polyethylenic backbone," be withdrawn.

In regards to the 35 U.S.C. §112 rejection of dependent claims 16-18, 42-44, 85-87, and 110-114, the amended independent claims now specify that "the oxygen scavenging polymer comprises an ethylenic backbone and at least one cyclic olefinic pendant group." Oxygen scavenging polymers having these aspects are clearly disclosed in *haec verba* on page 8, lines 5-27, of the specification and were generally disclosed as potential aspects of oxygen scavenger utilized in all compositions, packaging articles, and methods of making the compositions in the present patent application. Additionally, these aspects of the oxygen scavenging polymer were detailed in original claims 5, 31, 74, and 94. Thus, these claims are supported by the specification as filed. Applicants respectfully request that the 35 U.S.C. §112 rejection of claims 16-18, 42-44, 85-87, and 110-114 be withdrawn.

##### 5. *Claim Rejections under 35 U.S.C. §103*

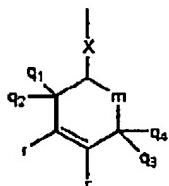
Claims 1-4, 6-11, 15, 17-30, 32-37, 41, 43-66, 70-73, 75-80, 84, 86-91, 93-98, 102-113 and 115 stand rejected under 35 U.S.C. §103(a) as being unpatentable over Bansleben et al., U.S. 6,255,248 ("Bansleben") in view of Cahill et al., U.S. 6,083,585 ("Cahill"). Specifically, the referenced section of the paragraph bridging pages 3 and 4 of the first Office Action dated March 13, 2002, asserts that Bansleben "discloses a multilayer package . . . containing an oxygen scavenging polymer and a diluent polymer such as PVDC . . ." and that "[t]he oxygen scavenger polymer includes 4-vinyl cyclohexene polymer . . ." Applicants respectfully traverse this rejection.

One condition to establish a *prima facie* case for obviousness is that the references must teach or suggest all of the claim limitations. Applicants respectfully submit that Bansleben in view of Cahill does not teach or suggest all the limitations of the present claims.

The present independent claims state that:

"the oxygen scavenging polymer comprises an ethylenic backbone and at least one cyclic olefinic pendant group having structure I:

09/575094US02  
09/666,642  
Art Unit: 1711



(I)

wherein  $q_1$ ,  $q_2$ ,  $q_3$ ,  $q_4$ , and  $r$  are independently selected from hydrogen, methyl, or ethyl;  $m$  is  $-(CH_2)_n-$ , wherein  $n$  is an integer from 0 to 4, inclusive;  $X$  is selected from:

$-O-(CHR)_n-$ ;  $-(C=O)-O-(CHR)_n-$ ;  $-NH-(CHR)_n-$ ;  $-O-(C=O)-(CHR)_n-$ ;  
 $-(C=O)-NH-(CHR)_n-$ ; or  $-(C=O)-O-CHOH-CH_2-O-$ ; and, when  $r$  is hydrogen, at least one of  $q_1$ ,  $q_2$ ,  $q_3$ , and  $q_4$  is also hydrogen."

Bansleben discloses an oxygen scavenging polymer produced from ethylene, cyclopentene, and vinyl cyclohexene (see Bansleben Examples). The polymer produced using vinyl cyclohexene would have a linking group,  $X$ , of null. Cahill discloses an oxygen scavenging polymer comprising a condensation polymer predominately made up of polyester segments and an oxygen scavenging amount of polyolefin oligomer segments (see Cahill Abstract, and column 6, lines 5-11). Cahill provides polypropylene, poly(4-methyl)1-pentene, and polybutadiene as examples of useful polyolefin oligomers that can be used in the oxygen scavenging copolycondensate (see Cahill column 10, lines 28-45), but does not disclose or suggest oxygen scavenging polymers having a cyclic olefinic pendent group. Therefore, the combination of Bansleben in view of Cahill cannot obviate the presently pending claims because the combination does not teach or suggest all the limitations of the independent claims. Specifically, Bansleben in view of Cahill does not teach or suggest the claimed oxygen scavenging polymer structure. Applicants respectfully request that the 35 U.S.C. §103(a) rejection of the claims over Bansleben in view of Cahill be withdrawn.

Claims 1-4, 6-11, 15, 17-30, 32-37, 41, 43-66, 70-73, 75-80, 84, 86-88, 90, 91, 93-98, 102-109 stand rejected under 35 U.S.C. §103(a) as being unpatentable over Gauthier et al., U.S. 6,313,241 ("Gauthier"). Specifically, page 3 of the Office Action dated June 24, 2005, asserts that "Gauthier discloses numerous examples of ethylene/vinyl cyclohexene copolymer in their Examples . . ." and that "films were co-extruded with the polymers . . . to laminate the polymer with material such as inherently

09/575094US02  
09/666,642  
Art Unit: 1711

24

oxygen barrier polymers such as ethylene vinyl alcohol in Example 37.” Applicants respectfully traverse this rejection.

Examples 34-41 of Gauthier teach forming a multilayer film by coextruding multiple layers. See Gauthier column 25, lines 55-56. Within Gauthier’s examples, the oxygen scavenging polymer and the oxygen barrier polymer are in separate layers of the film. In contrast, Applicants’ oxygen barrier composition comprises a blend of an oxygen barrier polymer and an oxygen scavenging polymer.

Another point of distinction between Gauthier and the present claims is the choice of the group which links the cyclic olefinic pendant group to the polymer backbone. Applicants, employ a linking group, X, selected from “-O-(CHR)<sub>n</sub>-; -(C=O)-O-(CHR)<sub>n</sub>-; -NH-(CHR)<sub>n</sub>-; -O-(C=O)-(CHR)<sub>n</sub>-; -(C=O)-NH-(CHR)<sub>n</sub>-; or -(C=O)-O-CHOH-CH<sub>2</sub>-O-.” Gauthier’s ethylene/vinyl cyclohexene copolymers have a linking group, X, of null.

Therefore, on two counts, Gauthier cannot obviate the present claims because Gauthier does not teach or suggest all the limitations of the pending claims. Applicants respectfully request that the 35 U.S.C. §103(a) rejection of the claims over Gauthier be withdrawn.

#### 6. *Request to Resubmit "Naga"*

The Office Action dated June 24, 2005, requested that the Applicants resubmit Naga *et al.*, *Macromol. Chem. Phys.* 2002, 203, 159-165 (“Naga”). Applicants respectfully resubmit Naga in order to complete the prosecution record of the present patent application.

#### 7. *Nonstatutory Double-Patenting Rejection*

Claims 1-4, 6-11, 15, 17-30, 32-37, 41, 43-66, 70-73, 75-80, 84, 86-91, 93-98, 102-113, and 115 have been rejected under the judicially created doctrine of obviousness-type double patenting as being unpatentable over claims 1-21 of U.S. Patent 6,525,123. Applicants respectfully traverse this ground for rejection; however, in the interest of furthering prosecution of this application, Applicants herein submit a terminal disclaimer directed to U.S. Patent 6,525,123 to overcome this rejection. Accordingly, Applicants respectfully request that the rejection of the claims under the judicially created doctrine of obviousness-type double patenting be withdrawn.

09/575094US02  
09/666,642  
Art Unit: 1711

25

8. *Final Remarks*

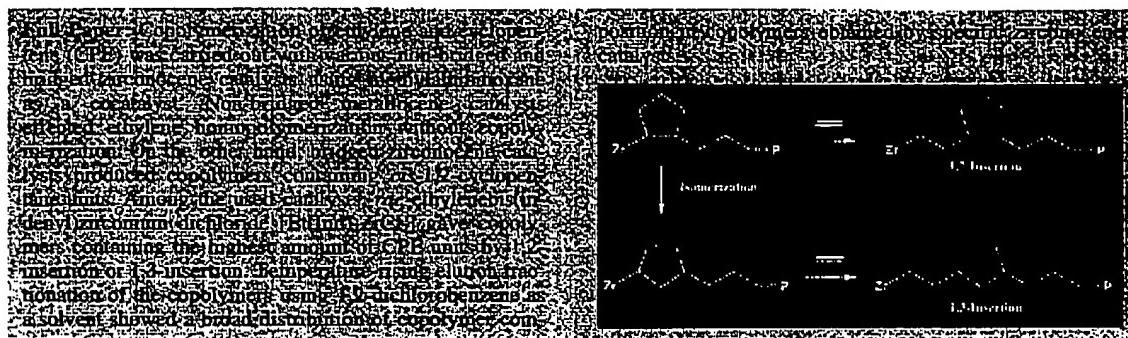
In conclusion, Applicants respectfully submit that all pending claims under consideration, claims 1-4, 7, 10-11, 15, 17-30, 33, 36-37, 41, 43-66, 70-73, 76, 79-80, 84, 86-91, 94, 97-98, 102-113, and 115 are in condition for allowance. The Examiner is invited to contact the undersigned patent attorney at (832) 813-4339 with any questions, comments or suggestions relating to the referenced patent application.

Respectfully submitted,



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## Copolymerization of Ethylene and Cyclopentene with Zirconocene Catalysts: Effect of Ligand Structure of Zirconocenes

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**Keywords:** copolymerization; cyclopentene; effect of ligand; ethylene; zirconocene catalyst

### Introduction

Metallocene catalysts are effective not only for the polymerization of common olefins, such as ethylene and propylene, but for the polymerization of cycloolefins.<sup>[1]</sup> Cycloolefins, such as cyclobutene and norbornene, can be polymerized via 1,2-propagation by some metallocene catalysts. On the other hand, cyclopentene is polymerized via a 1,3-insertion mechanism. The resulting polycycloolefins show extremely high melting points over 400°C.

Copolymerization of cycloolefin with ethylene or propylene is an effective method to control thermal properties of polycycloolefins.<sup>[2]</sup> Olefin copolymers containing cyclic structures have been developed for optical materials with high glass-transition temperature. Especially, poly(ethylene-*co*-norbornene) is a well-known and useful amorphous copolymer with high transparency. Kaminsky and Spiehl investigated the copolymerization of ethylene with monocyclic olefins, such as cyclopentene (CPE), cycloheptene and cyclooctene, with a zirconocene catalyst, *rac*-ethylenebis(indenyl)zirconium dichloride, combined with a cocatalyst methylaluminoxane (MAO).<sup>[3]</sup> They reported that cycloolefins were incorporated via 1,2-insertion mechan-

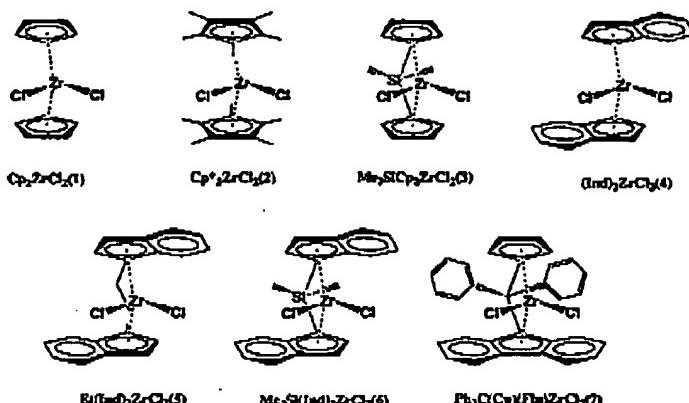
ism without a ring-opening reaction. Müller and coworkers investigated copolymerization of ethylene and CPE with a specific zirconocene catalyst, *rac*-dimethylsilylene(ferroceno[2,3]indenyl)cyclopentadienyl)zirconium dichloride, and detected 1,3-type CPE units in the resulting copolymer by detailed NMR studies.<sup>[4]</sup> The propagation mode of CPE in the copolymerization with ethylene undoubtedly affects the property of poly(ethylene-*co*-CPE). Control of CPE behaviors, that is, propagation mode and relative reactivity, in the copolymerization with ethylene should be essential for precise synthesis of poly(ethylene-*co*-CPE).

In this study, we carried out the copolymerization of ethylene and CPE with various zirconocene catalysts, investigating the effect of the ligand structure of zirconocene catalysts on the monomer reactivity and the mechanism of CPE polymerization.

### Experimental Part

#### Materials

Zirconocene catalysts were commercially obtained from Aldrich Co., Ltd. and Boulder Science Co., Ltd., and used without further purification. A list of zirconocene catalysts is



Scheme 1.

shown in Scheme 1. A hexane solution of methylisobutylaluminoxane (MMAO) was donated from Tosoh Akzo Co., Ltd. and used without further purification. CPE (Tokyo Kasei) was dried with  $\text{CaH}_2$ . Ethylene (Sumitomo Seika) was purified by passing it through columns of  $\text{NaOH}$ ,  $\text{P}_2\text{O}_5$  and molecular sieves 3 Å.

#### Copolymerization

The copolymerization of ethylene and CPE was carried out in a 100 mL glass reactor equipped with a magnetic stirrer. Toluene was added to the reactor under nitrogen atmosphere. Ethylene was introduced into the reactor at 40°C under 1 atm until the solvent was saturated with ethylene, and a measured amount of CPE was added. MMAO and a zirconocene catalyst were premixed in a 50 mL glass flask at 25°C within 5 min. Polymerization was started by introducing the catalyst solution into the reactor. The polymerization was terminated by adding a small amount of ethanol. The polymer obtained was extracted with boiling 1,2-dichlorobenzene to remove catalyst residues. The solution of extracted polymer was concentrated by evaporation and precipitated in a large excess of ethanol. The precipitate was recovered by filtration and dried in vacuo at 60°C for 6 h.

#### Analytical Procedures

Molecular weight and molecular weight distribution of the copolymer were measured at 140°C by means of gel permeation chromatography (Tosoh HLC-8121 GPC/HT) using 1,2-dichlorobenzene as a solvent and calibrated with standard polystyrene samples.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at 130°C on a JEOL Lambda-400 Fourier transform NMR spectrometer in 5 wt-% trichlorobenzene/benzene- $d_6$  (9/1, v/v). Melting temperatures were measured by a Seiko DSC6200 (Seiko Instruments Inc.) at a heating rate of 10 K/min after preheating to 200°C following precooling to -150°C. Temperature-rising elution fractionation (TREF) was carried out with cross fractionation chromatography (Dia-instruments CFCT-150C) using 1,2-dichlorobenzene as a solvent.

#### Results and Discussion

Copolymerization of ethylene and CPE was carried out with various zirconocene catalysts using MMAO as a cocatalyst at 40°C. Results of the copolymerization are summarized in Table 1. When the copolymerization was carried out with non-bridged zirconocene catalysts, 1, 2 and 4, polyethylene without incorporation of CPE was obtained. On the other hand, bridged zirconocene catalysts produced copolymers in good yields. The CPE content in the copolymer, which was determined by  $^1\text{H}$  NMR spectroscopy, increased with increasing CPE in the feed. The structure of inserted CPE units in the copolymers was investigated by  $^{13}\text{C}$  NMR spectroscopy. Figure 1 (a) and (b) show the  $^{13}\text{C}$  NMR spectra of the copolymers with low CPE content obtained with isospecific catalysts 5 and 6, respectively. Scheme 2 illustrates the structures of the copolymer corresponding to the  $^{13}\text{C}$  NMR spectra in Figure 1 (a) and (b). The signals at 43.3 (1, 2), 31.2 (3, 5), and 23.2 (4) ppm are assigned to isolated *cis*-1,2-cyclopentane units in the ethylene sequence.<sup>[3,4,5]</sup> Other signals are observed in the spectrum of a copolymer prepared by 5 (Figure 1 (a)). Those at 41.1 (2'), 40.6 (1',3'), and 32.2 (4',5') ppm are assignable to the isolated *cis*-1,3-cyclopentane units.<sup>[5]</sup> The 1,3-substituted cyclopentane structure can be explained by isomerization of 1,2-substituted cyclopentane terminal preceding ethylene insertion, as shown in Scheme 3. This mechanism is similar to the 1,3-type polymerization of propylene with some metallocene catalysts.<sup>[6]</sup> Copolymer obtained with aspecific catalyst 3 and syndiospecific catalyst 7 contained only *cis*-1,2-cyclopentane structure. These results indicate that the preferential mode of CPE polymerization is 1,2-type and that stereospecificity of the zirconocene catalysts does not affect the polymerization mode of CPE in the copolymerization.

Figure 2 shows the copolymer composition curves of ethylene/CPE copolymers obtained with bridged zircono-

Table 1. Results of ethylene/cyclopentene(CPE) copolymerization with zirconocene catalysts. Polymerization conditions: MMAO[Al]/[Zr], 1000; ethylene, 1.0 atm; polymerization temperature, 40°C.

Run	Catalyst		CPE mol/L	Time min	Polymer yield kg/mol Zr·h	CPE in copolymer <sup>a)</sup> mol-%	1,3-Insertion CPE units <sup>b)</sup> %	$M_n \times 10^{-4}$ <sup>c)</sup>	$M_w/M_n$ <sup>d)</sup>	$T_m$ <sup>e)</sup> °C
	Nature	mmol/L								
1	1	0.04	1.14	20	1340	0.0	-			
2	2	0.1	0.57	10	1560	0.0	-			
3	3	0.1	0.57	10	1090	2.1	0.0	2.7	3.3	
4		0.1	1.14	30	440	3.1	0.0	2.1	3.6	123.9, 103.1
5		0.2	2.27	45	220	6.5	0.0	1.1	2.7	
6		0.2	5.68	120	16.4	24.6	17.3			
7	4	0.1	0.57	6	1220	0.0	-			
8	5	0.1	0.23	6	1670	4.4	23.5	4.0	3.5	
9		0.1	0.45	6	2270	6.2	24.1	3.9	3.2	119.2, 75.7
10		0.1	0.57	5	4430	15.1	26.2	2.5	2.6	
11		0.1	1.14	5	4810	22.3	31.2	2.1	3.0	
12		0.1	2.27	6	4980	32.2	23.9	1.0	5.1	
13		0.1	5.68	15	1540	37.8	9.5	0.44	3.2	
14	6	0.04	0.57	20	2340	3.5	0.0	13.3	2.6	102.8
15		0.04	1.14	30	1230	4.8	0.0	7.2	2.3	
16		0.04	2.27	10	6720	12.9	0.0	5.8	1.9	
17		0.1	5.68	12	1840	27.5	5.6			
18	7	0.1	0.57	15	900	2.5	0.0	4.8	2.0	106.9
19		0.1	1.14	15	920	6.1	0.0	7.3	1.9	
20		0.1	2.27	60	340	13.4	0.0	6.5	1.8	
21		0.2	5.68	180	28.1	22.4	6.2	1.4	2.2	

<sup>a)</sup> Determined by <sup>1</sup>H NMR spectroscopy.

<sup>b)</sup> Determined by <sup>13</sup>C NMR spectroscopy.

<sup>c)</sup> Determined by GPC using polystyrene standard.

<sup>d)</sup> Measured by DSC.

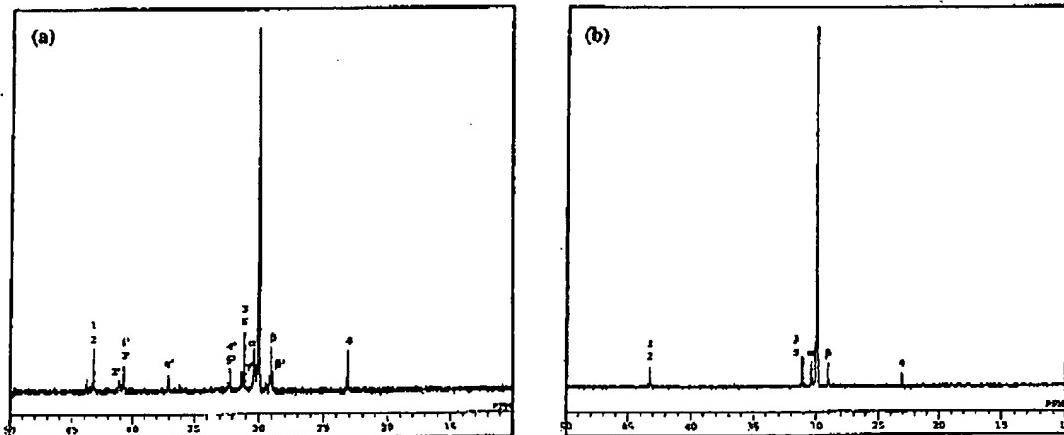
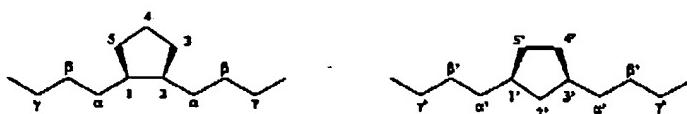


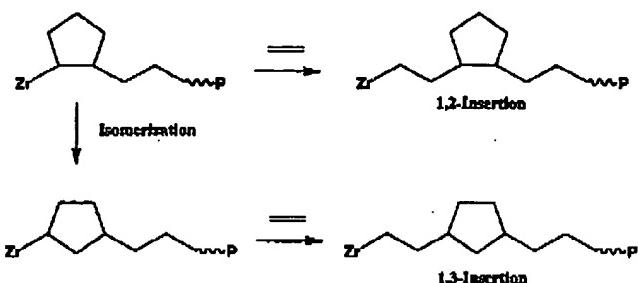
Figure 1. <sup>13</sup>C NMR spectra of poly(ethylene-co-CPE) obtained with bridged zirconocene catalysts: (a) 5 (Run 10). (b) 6 (Run 15).

cene catalysts. Ethylene is more reactive than CPE and the highest incorporation of CPE was attained in the copolymerization with the catalyst 5. Monomer reactivity ratios were determined by the Fineman-Ross plot,  $r_E$  being 239 (3), 21.9 (5), 143 (6), and 235 (7).

The copolymerization of ethylene and CPE was carried out at high CPE feed to obtain CPE-rich copolymers (Runs 6, 12, 13, 17, and 21). Monomer sequence distributions of the resulting copolymers with high CPE content (more than 20 mol-%) were investigated by <sup>13</sup>C NMR



Scheme 2.



Scheme 3.

Table 2. Monomer sequence distribution of poly(ethylene-*co*-CPE) obtained with bridged zirconocene catalysts. E = ethylene, C = CPE.

Run	Catalyst	CPE mol-%	EEE	EEC + CEE	ECE	CEC	ECC + CCE	CCC	EE	EC	CC
6	3	24.6	0.394	0.341	0.134	0.019	0.112	0.0	0.564	0.379	0.056
12	5	32.2	0.133	0.446	0.322	0.099	0.0	0.0	0.356	0.644	0.0
13	5	37.8	0.088	0.551	0.308	0.040	0.014	0.0	0.363	0.630	0.007
17	6	27.5	0.243	0.446	0.239	0.030	0.043	0.0	0.446	0.506	0.048
21	7	22.4	0.320	0.464	0.224	0.0	0.0	0.0	0.552	0.448	0.0

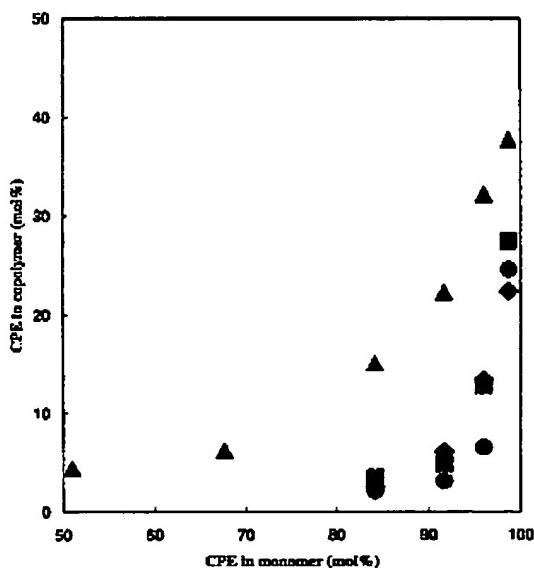


Figure 2. Copolymerization diagrams of ethylene and CPE with bridged zirconocene catalysts: 3 (●), 5 (▲), 6 (○), 7 (△).

spectroscopy, and the results are presented in Table 2. [CCC] sequence, where C represents CPE unit, was not detected in any copolymers, and [CC] dyad was not found in copolymers obtained with the catalysts 5 and 7. These results indicate that it is difficult to react the CPE monomer with a CPE growing end. This tendency becomes clearer in copolymerizations with the catalysts 5 and 7.

Figure 3 shows the relationship between CPE content and the molar content of 1,3-disubstituted cyclopentane unit in the copolymer. The 1,3-disubstituted cyclopentane units are detected in the copolymers containing more than 20 mol-% of CPE which were obtained with the catalysts 3, 6 and 7. When the copolymerization was carried out under low CPE feed using the same catalysts, 1,3-insertion did not occur. These results indicate that isomerization of 1,2-substituted cyclopentane terminal to 1,3-substituted one proceeds only at high CPE feed, in other words, low ethylene feed, as illustrated in Scheme 2. The content of 1,3-substituted cyclopentane units should increase with decreasing ethylene feed or with increasing CPE feed.

The catalyst 5 showed peculiar behaviors in the copolymerization of ethylene and CPE that the content of 1,3-disubstituted cyclopentane units was fairly high in the

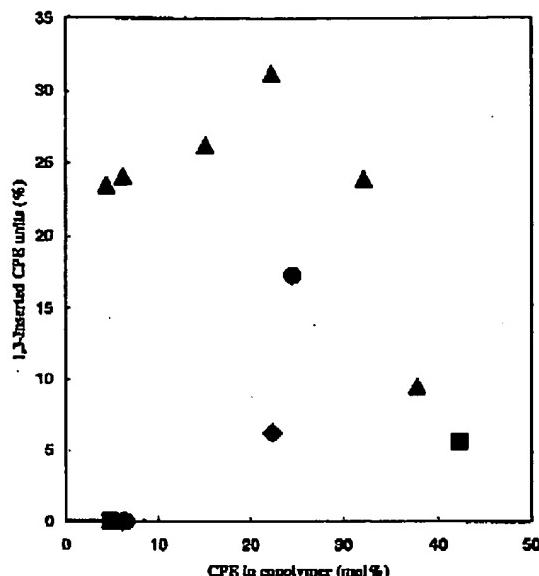
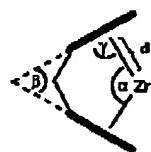
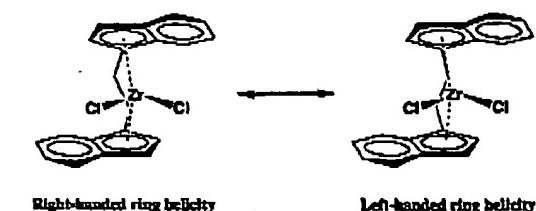


Figure 3. Relationship between CPE content and molar content of 1,3-disubstituted cyclopentane unit in the copolymer obtained with bridged zirconocene catalysts 3 (●), 5 (▲), 6 (■), and 7 (◊).



Scheme 4.

copolymers obtained under low CPE feed conditions and, after reaching the maximum content, decreased sharply with increasing CPE content in the copolymer. The sym-



Scheme 5.

metry of bridged zirconocene catalysts may play an important role in determining the reactivity and mechanism of CPE insertion. To test this possibility, crystallographic parameters were compared: 5;  $\alpha = 125.3^\circ$ ,  $\beta = 60.4^\circ$ ,  $\gamma = 87.2^\circ$ ,  $d(\text{Zr-Cp}) = 2.44\text{--}2.62 \text{ \AA}$ ;<sup>[7]</sup> 6;  $\alpha = 127.8^\circ$ ,  $\beta = 60.2^\circ$ ,  $\gamma = 85.7^\circ$ ,  $d = 2.46\text{--}2.66 \text{ \AA}$ ,<sup>[8]</sup> where  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $d$  are angle of cp-Zr-cp' (cp, cp' = centroids of the Cp rings, Cp = cyclopentadienyl moiety in the indenyl ligand), angle between Cp planes, angle between Cp plane and cp-Zr bond, and length of cp-Zr, respectively, as shown in Scheme 4. The catalyst 5 shows a somewhat smaller  $\alpha$  angle and a larger  $\gamma$  angle than those of the catalyst 6. This difference means that the coordination space of the catalyst 5 is wider than that of the catalyst 6. Another possibility is a distortion of indenyl ligands of the catalyst 5 due to internal rotation of the ethylidene bridge. The catalyst 5 forms either right-handed or left-handed ring helix (Scheme 5) as reported by Kaminsky et al.<sup>[9]</sup> The internal rotation between right-hand and left-hand structure widens  $\beta$  and  $\gamma$  angles and narrows  $\alpha$  angle. The rotation leaves wider coordination space in the catalyst 5. However, the facile 1,3-insertion of CPE by the catalyst 5 can not be explained in this way.

Thermal properties of the copolymers with low CPE content were investigated. Multiple melting endotherms were observed in the copolymers obtained with the cata-

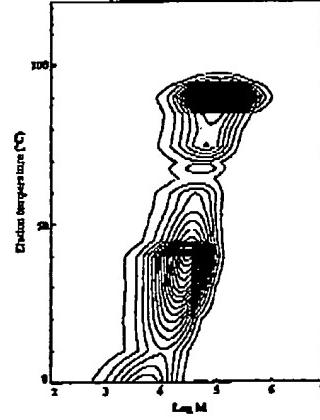
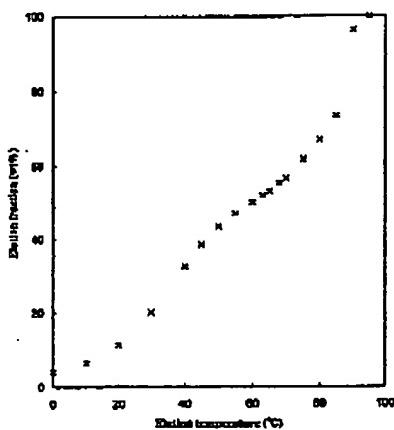


Figure 4. TREF and CFC diagrams of poly(ethylene-co-CPE) obtained with the catalyst 5 (Run 9).

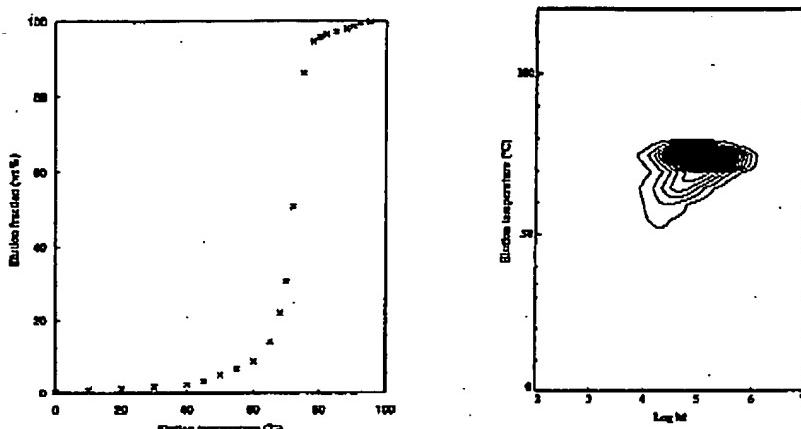


Figure 5. TREF and CFC diagrams of poly(ethylene-*co*-CPE) obtained with the catalyst 6 (Run 14).

lysts 3 and 5. TREF of the copolymers was measured with CFC-IR to elucidate the composition distribution of the copolymers. Figure 4 and 5 show the TREF diagrams together with contour-type CFC diagrams of the copolymers obtained with the catalysts 5 and 6, respectively. Figure 4 indicates that the copolymer obtained with the catalyst 5 is composed of three types of polymers; the first is extracted below 10°C, the second from 10°C to 70°C, and the third above 70°C. The structures of ODCB-elution fractions below and above 70°C were investigated by NMR spectroscopy. The CPE contents of the low temperature (below 70°C) and high temperature (above 70°C) elution fractions were 9.9 mol-% and 2.9 mol-%, respectively. The contents of 1,3-disubstituted CPE units of both fractions were almost the same. The difference of elution temperature is derived from the difference of the CPE content. On the other hand, the copolymer obtained with the catalyst 6 was extracted around 80°C as shown in Figure 5, and a narrow distribution of the copolymer composition was confirmed.

Metallocene catalysts have been shown to produce uniform active species and to produce polyolefins with narrow distribution of molecular weight and composition. However, Soga et al. found a heterogeneous composition of poly(ethylene-*co*-1-hexene) obtained with typical metallocene catalysts.<sup>[10]</sup> The active species of metallocene-MAO systems have been analyzed by various methods, and some kinds of active species have been detected. Cam et al. observed reduction of Zr(IV) to Zr(III) in 1-MAO system.<sup>[11]</sup> Tricio et al. detected two kinds of ion pairs, i.e., monomeric and dimeric ones, in the Cp<sub>2</sub>TiCH<sub>3</sub>Cl-MAO system.<sup>[12]</sup> It is considered that a heterogeneous composition of the copolymer prepared by a metallocene catalyst should be derived from heterogeneity of the active sites in the copolymerization. The same

explanation could be applied to the poly(ethylene-*co*-CPE) obtained with the catalysts 3 and 5. A further study is, however, necessary to clarify the relationship between molecular structure of zirconocene and distribution of copolymer composition.

### Conclusion

Poly(ethylene-*co*-CPE) was successfully obtained with bridged zirconocene catalysts. The CPE was preferentially incorporated via 1,2-insertion. The catalyst 5 gave the copolymer with the highest content of CPE incorporated by 1,3-insertion. TREF of the copolymers showed the distribution of copolymer composition obtained with the catalysts 3 and 5.

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